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Synthesis and reactivity of palladium and platinum complexes containing the bis(diphenylphosphino)methanide ligand

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Abstract

Complexes of general formulae $[M(C_6X_5)(Ph_2PCHPPh_2)(L)]$ (M = Pd, Pt; X = F, Cl; L = PR_3, dppm($Ph_2PCH_2PPh_2$)) have been obtained either by reaction of $MCl(C_6F_5)(PR_3)_2$ with dppm and NaH or with dppm–Li or reaction of $[M(C_6F_5)(dppm)(PR_3)](ClO_4)$ with NaH. The complexes $M(C_6X_5)(acac)(L)$ react with dppm to give analogous ddppm $\{[Ph_2PCHPPh_2]^-\}$ derivatives. Treatment of these complexes with HBF_4 gives of the corresponding dppm cationic derivatives. The complexes have been characterized by IR, ^{19}F NMR, and $^{31}P(^1H)$ NMR spectroscopy.

Introduction

We previously studied the synthesis and reactivity of mononuclear and dinuclear perhalophenyl derivatives of Pd^{II}, Pt^{II}, Pd^{I} and Pt^{I} containing bis(diphenylphosphino)methane (dppm) as a neutral ligand [1]. It has been known for several years that the CH_2 group of dppm can be deprotonated by strong bases to give the anion bis(diphenylphosphino)methanide $[(Ph_2P)_2CH]^-$ (ddppm), and that this anion is itself a good ligand [2,3]. This ligand (ddppm) has received attention recently in the coordination chemistry of Pd^{II} and Pt^{II} [4–9]. We have now used several routes to make mononuclear pentahalophenyl derivatives of Pd^{II} and Pt^{II} containing the $[(Ph_2P)_2CH]^-$ group acting as P–P bidentate ligand. The interconversion of the coordinated dppm and ddppm ligands has also been studied.

Results and discussion

Analytical and relevant IR absorptions are listed in Table 1, and $^{31}P(^1H)$ and ^{19}F NMR parameters are summarized in Tables 2 and 3, respectively.

Table 1

Analytical and relevant IR data (cm^{-1}).

Complexes	Analyses (found (calcd.) (%))		IR	
	C	H	C_6X_5 [a]	ddppm
$Pd(C_6F_5)(Ph_2PCHPPh_2)(PPh_3)$ (I)	63.98 (64.03)	3.80 (3.94)	770	900,870
$Pd(C_6F_5)(Ph_2PCHPPh_2)(PPh_2Et)$ (II)	61.85 (62.04)	4.13 (4.16)	775	895,855
$Pd(C_6F_5)(Ph_2PCHPPh_2)(PPh_2Me)$ (III)	62.65 (61.66)	4.28 (3.99)	770	895,855
$Pt(C_6F_5)(Ph_2PCHPPh_2)(PPh_3)$ (IV)	58.36 (58.39)	4.07 (3.60)	780	905,855
$Pt(C_6F_5)(Ph_2PCHPPh_2)(PPh_2Et)$ (V)	56.52 (56.31)	4.12 (3.78)	780	895,840
$Pd(C_6Cl_5)(Ph_2PCHPPh_2)(PPh_2Me)$ (VI)	56.84 (56.26)	3.77 (3.64)	830,610 [b]	890,870
$Pd(C_6Cl_5)(Ph_2PCHPPh_2)$(dppm-*P*) (VII)	59.66 (59.86)	3.87 (3.85)	825,610 [b]	895,870
$Pt(C_6F_5)(Ph_2PCHPPh_2)$(dppm-*P*) (VIII)	58.52 (59.52)	4.03 (3.83)	785	900,865
$[Pd(C_6F_5)(Ph_2PCH_2PPh_2)(PPh_3)](BF_4)$ (IX)	58.33 (58.44)	3.95 (3.70)	790	
$[Pd(C_6F_5)(Ph_2PCH_2PPh_2)(PPh_2Et)](BF_4)$ (X)	56.61 (56.36)	3.73 (3.89)	780	
$[Pd(C_6F_5)(Ph_2PCH_2PPh_2)(PPh_2Me)](BF_4)$ (XI)	55.38 (55.93)	4.06 (3.73)	770	
$[Pt(C_6F_5)(Ph_2PCH_2PPh_2)(PPh_3)](BF_4)$ (XII)	53.45 (53.71)	3.67 (3.40)	790	
$[Pd(C_6F_5)(Ph_2PCH_2PPh_2)(tht)](ClO_4)$ (XIII)	49.74 (49.72)	3.73 (3.57)	780	
$[Pd(C_6F_5)(Ph_2PCH_2PPh_2)(PPh_3)](ClO_4)$ (XIV)	57.68 (57.72)	4.11 (3.65)	780	
$Pd(C_6Cl_5)$(acac)(dppm-*P*) (XV)	52.29 (51.52)	4.17 (3.48)	835,645 [b]	

[a] X-sensitive absorption. [b] ν(M–C) bond.

Synthesis of the complexes

Neutral palladium complexes of the type $[Pd(C_6F_5)(Ph_2PCHPPh_2)(PR_3)]$ (**A**) containing the *P*,*P'*-chelating ligand bis(diphenylphosphino)methanide have been obtained by various routes, which are summarized in Scheme 1.

Route 1a. Reaction of the $PdCl(C_6F_5)(PR_3)_2$ derivatives in THF with dppm in the presence of NaH results in deprotonation of the CH_2 group of the dppm ligand.

Route 1b. The reaction of a THF solution of $Li(Ph_2PCHPPh_2)$ (prepared in situ by reacting dppm and ^nBuLi) with $PdCl(C_6F_5)(PR_3)_2$ gives complexes of type **A**.

Route 1c. The acetylacetonate complexes $Pd(acac)(C_6F_5)(PR_3)$ react with dppm in CH_2Cl_2 at room temperature to yield the corresponding ddppm derivatives (type **A**, Scheme 1) and acacH. This process was unexpected in view of the relative acidities of acacH and dppm, which have pK_a values of 9.0 and 29.9, respectively [10,11]. The occurrence of the reaction can probably be attributed to electronic effects; the Pd^{II} is a class b metallic centre, and process 1c involves substitution of a

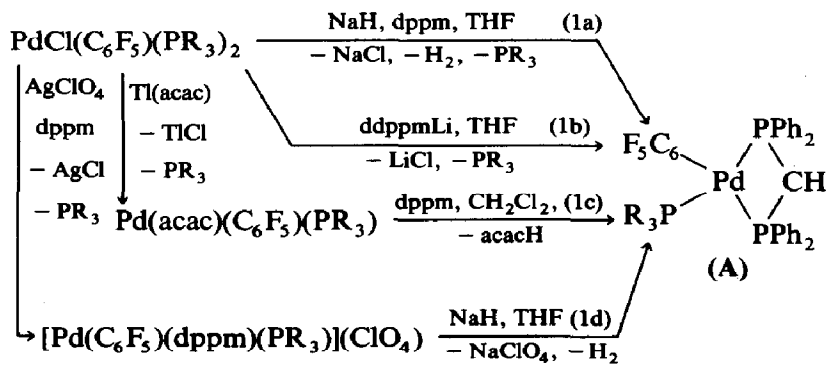
Table 2

$^{31}P(^{1}H)$ NMR [a] data (δ (ppm), J (Hz))

	I	II	III	IV	V	VI	VII	VIII	XV
PR_3 δP_A	23.6	18.2	6.7	18.3	13.2	5.9			
ddppm									
δP_B	−36.7	−38.0	−40.9	−41.8	−42.7	−42.4	−43.6	−43.4	
δP_C	−44.1	−42.6	−45.7	−47.3	−46.7	−43.8	−44.3	−48.0	
dppm									
δP_D							−30.6	−28.9	−28.2
δP_E							16.3	10.7	23.8
$^{2}J(P_A-P_B)$	390	392	400	369	365	392			
$^{2}J(P_A-P_C)$				10	10	20			
$^{2}J(P_B-P_C)$	56	58	57	15	17	52	50		
$^{2}J(P_B-P_E)$							386	368	
$^{2}J(P_C-P_E)$							15	7	
$^{2}J(P_D-P_E)$							30	40	47
$^{4}J(P_B-P_D)$							11		
$^{1}J(Pt-P_A)$				2468	2420				
$^{1}J(Pt-P_B)$				2061	1998			1980	
$^{1}J(Pt-P_C)$				1780	1802			1764	
$^{1}J(Pt-P_E)$								2427	

	IX	X	XI	XII	XIII	XIV
PR_3 δP_A	23.9	19.9	7.6	17.1		24.0
dppm						
δP_F	−26.6	−26.4	−28.8	−36.0	−26.5	−26.6
δP_G	−34.4	−34.0	−34.9	−40.9	−42.8	−34.8
$^{2}J(P_A-P_F)$	398	398	406	370		401
$^{2}J(P_A-P_G)$	5		10	13		
$^{2}J(P_F-P_G)$	68	63	69	51	77	67
$^{1}J(Pt-P_A)$				2534		
$^{1}J(Pt-P_F)$				2129		
$^{1}J(Pt-P_G)$				1814		

[a] In $CDCl_3$ values relative to external 85% H_3PO_4.



Scheme 1

Table 3

^{19}F NMR [a] data (δ (ppm), J Hz))

	$\delta(F_o)$	$\delta(F_m)$	$\delta(F_p)$	$\delta(BF_4)$	$^3J(Pt-F_o)$
I	−112.9	−162.9	−162.1		
II	−112.6	−162.9	−161.7		
III	−112.4	−163.0	−161.9		
IV	−115.0	–	–		282
V	−117.5	−165.4	−163.7		282
VIII	−117.6	−165.5	−163.8		281
IX	−117.3	−162.0	−159.7	−153.1	
X	−116.3	−161.4	−158.3	−153.2	
XI	−116.7	−161.6	−158.7	−153.1	
XII	−119.0	−163.1	−160.7	−153.2	278
XIII	−117.5	−160.9	−157.1		
XIV	−117.1	−161.8	−159.5		

[a] In $CDCl_3$ values relative to external $CFCl_3$.

O,O'-donor by a *P,P'*-donor ligand [12]. This type of process has been reported previously [6]

Route 1d. Cationic complexes $[Pd(C_6F_5)(dppm)(PR_3)](ClO_4)$ are deprotonated by NaH in THF under mild conditions.

The pentachlorophenyl derivative $Pd(C_6Cl_5)(Ph_2PCHPPh_2)(PPh_2Me)$ (VI) has been obtained by route 1c (Scheme 1) by using $Pd(C_6Cl_5)(acac)(PPh_2Me)$ as starting material. Complex VI can also be obtained by treating $Pd(C_6Cl_5)(acac)$(dppm-*P*) with PPh_2Me (molar ratio 1/1) in CH_2Cl_2 at room temperature (eq. 1).

$$Pd(C_6Cl_5)(acac\text{-}O,O')(dppm\text{-}P) + PPh_2Me \rightarrow Pd(C_6Cl_5)(ddppm)(PPh_2Me) + acacH \quad (1)$$

Perfluorophenyl derivatives of Pt^{II} $Pt(C_6F_5)(Ph_2PCHPPh_2)(PR_3)$ ($PR_3 = PPh_3$ (IV), PPh_2Et (V)) were obtained by methods 1a, 1c and 1d from the appropriate starting materials. Complex V was also made by treating $Pt(C_6F_5)(acac)(tht)$ with dppm and PPh_2Et in CH_2Cl_2 at room temperature, as in eq. 2.

$$Pt(C_6F_5)(acac\text{-}O,O')(tht) + dppm + PPh_2Et \rightarrow Pt(C_6F_5)(ddppm)(PPh_2Et) + acacH + tht \quad (2)$$

Some Pd^{II} or Pt^{II} perhalophenyl complexes containing both the monodentate dppm and chelate ddppm ligands were obtained by routes 2a,b,c of Scheme 2.

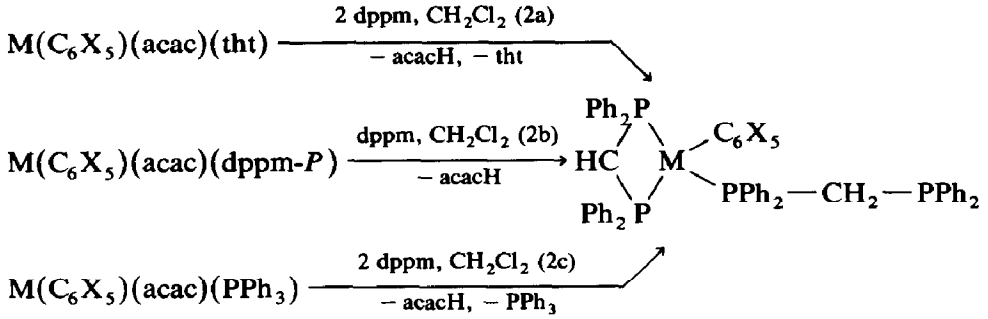
Routes 2a, b and c (Scheme 2) involve the elimination of the acetylacetonate ligand as acacH and coordination of the deprotonated dppm as a chelated ligand. With 2a and 2c the monodentate neutral ligand is replaced by a dppm group in monodentate mode (dppm-*P*).

The syntheses of the complexes $[Pd(C_6F_5)(dppm)(tht)](ClO_4)$ (XIII), $[Pd(C_6F_5)(dppm)(PPh_3)](ClO_4)$ (XIV) and $Pd(C_6Cl_5)(acac)$(dppm-*P*) (XV), used as starting materials, are described in the Experimental section.

As expected, complexes containing ddppm react with HBF_4 in Et_2O to give the corresponding dppm derivatives (eq. 3), in keeping with the basic character of the carbon atom of the methanide group.

$$M(C_6F_5)(ddppm)(PR_3) + HBF_4 \rightarrow [M(C_6F_5)(dppm)(PR_3)](BF_4) \quad (3)$$

(M = Pd; $PR_3 = PPh_3$ (IX), PPh_2Et (X), PPh_2Me (XI); M = Pt; $PR_3 = PPh_3$ (XII))



(M = Pd, $C_6X_5 = C_6Cl_5$ (VII); M = Pt, $C_6X_5 = C_6F_5$ (VIII))

Scheme 2

Even so we were unable to obtain binuclear derivatives by making use of the residual electronic density on the CH group of ddppm ligand in our complexes. No reaction took place between $Pd(C_6F_5)(PPh_3)$(ddppm) and $O_3ClOAgPPh_3$ in anhydrous OEt_2, the starting materials being recovered after 2 h at room temperature. On the other hand, from the reaction between $Pd(C_6F_5)(PPh_3)$(ddppm) and $Pd(OClO_3)(C_6F_5)(PPh_3)_2$ in benzene (4 h) we were able to isolate $[Pd(C_6F_5)(PPh_3)$-(dppm)$](ClO_4)$ but no binuclear derivatives. These results are in contrast with the well known ability of the ddppm ligand to act as a tridentate ligand by using not only its *P*-donor atoms but also the C atoms of the methanide group [13–16].

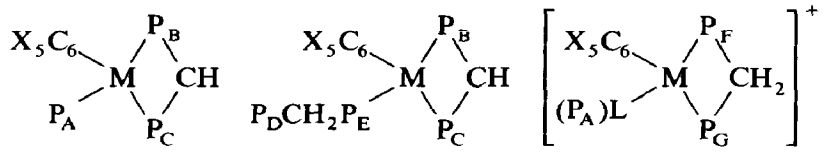
IR, ^{19}F and $^{31}P(^1H)$ NMR

All the IR spectra of the pentafluorophenyl derivatives show characteristics bands of the C_6F_5 group [17] near 1510, 1050, and 950 cm^{-1}. The pentachlorophenyl derivatives show absorptions due to the C_6Cl_5 group (1290–1230 cm^{-1} region and ca. 620 cm^{-1}) [18,19]. Complexes IX–XII exhibit a strong and broad absorption at ≈ 1060 cm^{-1} due to the counter ion BF_4^- [20].

In any of two coordination modes of the dppm (monodentate or chelate) this ligand shows characteristic absorptions in the range 520–410 cm^{-1}, but an extra absorption of medium to strong intensity in the range 550–530 cm^{-1} is observed when the dppm acts as a chelating ligand. The $[Ph_2PCHPPh_2]^-$ group shows, in addition to the characteristic absorptions in the 550–400 cm^{-1} area, two strong absorptions in the 900–850 cm^{-1} region that seem to be characteristic vibrations of the methanide P–CH–P system [5].

The chemical shifts and *J*(P–P) and *J*(Pt–P) values (see Table 2) from the ^{31}P NMR spectra provide valuable information about the various P atoms in the PR_3 or diphosphine groups. For the complexes I–XV, we can distinguish several types of P atoms:

(a) P_A, P atom of the coordinated PR_3;
(b) P_B, P atom *trans* to a PR_3 group of the ddppm ligand;
(c) P_C, P atom *trans* to a C_6X_5 group of the ddppm ligand;
(d) P_D, uncoordinated P atom of the monodentate dppm ligand;
(e) P_E, coordinated P atom of the monodentate dppm ligand;
(f) P_F, P atom *trans* to L of the chelate dppm ligand;
(g) P_G, P atom *trans* to C_6F_5 of the chelate dppm ligand.



The P atoms of PR_3 (P_A) show positive ^{31}P chemical shifts (24 to 5 ppm). The signal due to P_A in $Pd^{(II)}$ derivatives appears at higher frequencies than that in the related $Pt^{(II)}$ complexes.

The P atoms of bidentate $[Ph_2PCHPPh_2]^-$ group (P_B, P_C) show high negative ^{31}P chemical shifts (−36 to −48 ppm). The signal from the P_C atom (*trans* to C_6X_5 group) appears at lower frequencies than that from the P_B atom (*trans* to a neutral PR_3 ligand). The values of $^2J(P_B-P_C)$ are ≈ 50 Hz in the $Pd^{(II)}$ complexes and smaller (≈ 15 Hz) in the $Pt^{(II)}$ compounds. However, the $^2J(P_A-P_C)$ couplings are not observable for $Pd^{(II)}$ complexes but have values of ca. 10 Hz for the $Pt^{(II)}$ complexes.

The coordinated P atom in the monodentate dppm ligand (P_E) shows positive ^{31}P chemical shifts (16.3 ppm to VII, 10.7 ppm to VIII, 23.8 ppm to XV) in the region expected for monodentate PR_3 groups (P_A). The uncoordinated P atom in the dppm-P group (P_D) appears at negatives values, well removed from the P_E signals.

The P atoms of bidentate chelate $Ph_2PCH_2PPh_2$ group (P_F,P_G) show negative ^{31}P chemical shifts (−26 to −43 ppm), shifted upfield from the ^{31}P signal from the free dppm ligand ($\delta_p = -21.95$ ppm). The value of $\delta(P_G)$ (P_G *trans* to a C_6F_5 group) is more negative than that of $\delta(P_F)$ (P_F *trans* to a PR_3 group).

Finally, the ^{19}F NMR spectra of the pentafluorophenyl derivatives show three sets of signals corresponding to F_o (δ −112 to −120 ppm), F_p δ −157 to −163 ppm) and F_m (δ −160 to −165 ppm), in keeping with the presence of a C_6F_5 group freely rotating around the M–C bond.

Experimental

C and H analyses were carried out with a Perkin Elmer 240-B microanalyser. IR spectra were recorded (in the 4000–200 cm^{-1} range) on a Perkin Elmer spectrophotometer using Nujol mulls between polyethylene sheets. ^{19}F and $^{31}P(^1H)$ NMR spectra were recorded on a Varian XL-200 spectrometer. The complexes $PdCl(C_6F_5)(PR_3)_2$ ($PR_3 = PPh_3$, PPh_2Et, PPh_2Me), and $[M(\mu-Cl)(C_6X_5)(L)]_2$ (M = Pd, Pt; X = F, Cl; L = PPh_3, PPh_2Et, PPh_2Me, tht), (tht = tetrahydrothiophene) were prepared as described previously [19]. The complexes $[M(C_6X_5)(acac)(L)]$ (M = Pd, Pt; X = F, Cl; L = PPh_3, PPh_2Et, PPh_2Me, tht) were prepared by the method used for $Pd(C_6F_5)(acac)(PPh_3)$ [21].

Other starting materials were prepared as follows:

$[Pd(C_6F_5)(dppm)(tht)](ClO_4)$ (XIII)

To a solution of $[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ (0.387 g, 0.487 mmol) in 20 ml of acetone was added $AgClO_4$ (0.202 g, 0.974 mmol). The mixture, protected from the light, was stirred at room temperature for 15 min and the precipitated AgCl was removed. dppm (0.374 g, 0.974 mmol) was added to the solution, which was then evaporated

to dryness. The oily residue was stirred with Et_2O (10 ml) to give a pale-yellow solid XIII in 86% yield.

[Pd(C$_6$F$_5$)(dppm)(PPh$_3$)](ClO$_4$) (XIV)

This was obtained similarly from [Pd(μ-Cl)(C$_6$F$_5$)(PPh$_3$)]$_2$ in 75% yield.

Pd(C$_6$Cl$_5$)(acac)(dppm-P) (XV)

To a solution of [Pd(C$_6$Cl$_5$)(acac)(tht)] (0.15 g, 0.276 mmol) in 15 ml of dichloromethane was added dppm (0.106 g, 0.276 mmol). The mixture was stirred for 15 min at room temperature then evaporated to dryness, and the residue was treated with n-hexane (20 ml) to give an orange solid XV in 77% yield.

Pd(C$_6$F$_5$)(Ph$_2$PCHPPh$_2$)(PPh$_3$) (I)

Method a: From PdCl(C$_6$F$_5$)(PPh$_3$)$_2$ with NaH as deprotonating agent. To a suspension of 0.2 gr of NaH in 20 ml of THF were added dppm (0.192 g, 0.5 mmol) and PdCl(C$_6$F$_5$)(PPh$_3$)$_2$ (0.416 g, 0.5 mmol). The mixture was stirred for 16 h at room temperature under N_2, then filtered, and the filtrate was evaporated to dryness and the oily residue stirred with Et_2O (10 ml) to give an orange solid I in 70% yield.

Method b: From PdCl(C$_6$F$_5$)(PPh$_3$)$_2$ using ^{n}BuLi as deprotonating agent. To a solution of dppm (0.57 g, 1.50 mmol) in 10 ml of benzene was added ^{n}BuLi (2 ml of 0.9 *N* solution in n-hexane, 1.8 mmol). The mixture was refluxed for 2 h under N_2 and PdCl(C$_6$F$_5$)(PPh$_3$)$_2$ (0.833 g, 1.00 mol) was then added. The mixture was stirred for 2 h at room temperature then filtered, and the filtrate was evaporated almost to dryness. Addition of $\approx$ 25 ml of Et_2O gave a pale-yellow solid and an orange-yellow solution, which was filtered and evaporated to dryness. Addition of 70 ml of n-hexane to the residue afforded I in 66% yield.

Method c: From Pd(C$_6$F$_5$)(acac)(PPh$_3$). To a solution of Pd(C$_6$F$_5$)(acac)(PPh$_3$) (0.120 g, 0.189 mmol) in 20 ml of dichloromethane was added dppm (0.072 g, 0.189 mmol). The initially pale-yellow solution turned orange. It was stirred for 30 min at room temperature then evaporated to ca. 3 ml, and n-hexane (10 ml) was added, to precipitate complex I in 73% yield.

Method d: From [Pd(C$_6$F$_5$)(dppm)(PPh$_3$)](ClO$_4$). To a suspension of NaH (0.2 g) in 25 ml of Et_2O was added [Pd(C$_6$F$_5$)(dppm)(PPh$_3$)](ClO$_4$) (0.259 g, 0.254 mmol). The mixture was stirred under N_2 for 4 h at room temperature then filtered, and the filtrate evaporated almost to dryness. Addition of n-hexane (20 ml) afforded I in 74% yield.

Pd(C$_6$F$_5$)(Ph$_2$PCHPPh$_2$)(PR$_3$); PR$_3$ = PPh$_2$Et(II), PPh$_2$Me (III)

Similar procedures gave complexes II and III which were obtained by both methods a and c.

Pt(C$_6$F$_5$)(Ph$_2$PCHPPh$_2$)(PR$_3$) (PR$_3$ = PPh$_3$ (IV), PPh$_2$Et (V))

Complex IV was obtained by methods a, c, and d from PtCl(C$_6$F$_5$)(PPh$_3$)$_2$, Pt(C$_6$F$_5$(acac)(PPh$_3$) and [Pt(C$_6$F$_5$)(dppm)(PPh$_3$)](BF$_4$), respectively. Complex V was obtained by method a, and also as follows:

To a solution of Pt(C$_6$F$_5$)(acac)(tht) (0.142 g, 0.259 mmol) in 20 ml of CH_2Cl_2 was added dppm (0.100 g, 0.259 mmol), to give a yellow solution, to which PPh_2Et (55 μl, 0.259 mmol) was added. The mixture was stirred for 30 min at room

temperature then evaporated to dryness and the oily residue was stirred with Et_2O (10 ml) to give V in 78% yield.

$Pd(C_6Cl_5)(Ph_2PCHPPh_2)(PPh_2Me)$ (VI)

Method a: From $Pd(C_6Cl_5)(acac)(PPh_2Me)$. This was made by method 1c from $Pd(C_6Cl_5)(acac)(PPh_2Me)$ in 69% yield.

Method b: From $Pd(C_6Cl_5)(acac)(dppm\text{-}P)$. To a solution of $Pd(C_6Cl_5)(acac)$ (dppm-*P*) (0.25 g, 0.297 mmol) in 20 ml of CH_2Cl_2 was added PPh_2Me (59.7 μl, 0.297 mmol). The solution was stirred at room temperature for 2 h then evaporated to dryness. The residue was stirred with n-hexane (20 ml) to give the orange solid VI, in 71% yield.

$Pd(C_6Cl_5)(Ph_2PCHPPh_2)(Ph_2PCH_2PPh_2)$ (VII)

Method a: To a solution of $Pd(C_6Cl_5)(acac)(tht)$ (0.223 g, 0.410 mmol) in 15 ml of CH_2Cl_2 was added dppm (0.315 g, 0.821 mmol). The solution was stirred for 1 h at room temperature then evaporated to ca. 3 ml, and Et_2O (15 ml) was added to precipitate complex VII in 73% yield.

Method b: To a solution of $Pd(C_6Cl_5)(acac)$(dppm-*P*) (0.130 g, 0.155 mmol) in 20 ml of CH_2Cl_2, was added dppm (0.056 g, 0.155 mmol). The solution was stirred for 1 h at room temperature then evaporated to ca. 3 ml, and Et_2O was added to precipitate the complex VII, in 76% yield, as a yellow solid.

Method c: To a solution of $Pd(C_6Cl_5)(acac)(PPh_3)$ (0.100 g, 0.139 mmol) in 20 ml of CH_2Cl_2 was added, dppm (0.107 g, 0.278 mmol). The solution was stirred at room temperature for 30 min then evaporated almost to dryness, and Et_2O (20 ml) was added to precipitate complex VII in 40% yield.

$Pt(C_6F_5)(Ph_2PCHPPh_2)(Ph_2PCH_2PPh_2)$ (VIII)

Complex (VIII) was made by method a. (Scheme 2) from $Pt(C_6F_5)(acac)(tht)$. The reaction time was 6 h and the yield 78%.

$[M(C_6F_5)(Ph_2PCH_2PPh_2)(PR_3)](BF_4)$ ($M = Pd$: $PR_3 = PPh_3$ (IX), PPh_2Et (X), PPh_2Me(XI); $M = Pt$: $PR_3 = PPh_3$ (XII)

To a suspension of $Pd(C_6F_5)(Ph_2PCHPPh_2)(PPh_3)$ (0.184 g, 0.200 mmol) in 20 ml of Et_2O was added HBF_4 (0.2 mmol, 27 μl of a solution HBF_4/Et_2O 54%). The initially yellow-orange suspension turned white. After 30 min stirring at room temperature the precipitate was filtered off, washed with Et_2O, dried and identified as IX (80% yield).

Complexes X, XI and XII were obtained similarly. Yields: 81% (X), 64% (XI), and 85% (XII).

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